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First Stable and Persistent 1,3-Bisketene and Trisketene

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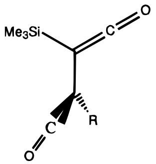
Bisketenes have been studied for 90 years,[1,2] and recent studies in our laboratories have taken advantage of the stabilization of ketenes by silyl substituents to prepare a variety of 1,2-bisketenes such as **1**, which have been shown to prefer the twisted conformation shown.[2d] Other types of bisketenes include the carbon monoxide dimer, O═C═C═O (**2**), which was sought by Staudinger and co-workers[1a] but is still unknown, even though calculations indicate it may be capable of existence,[1d] and carbon suboxide (**3**), the first bisketene which was prepared.[1b] The species **2** and **3** may be classified as 0,0- and 1,1-bisketenes, respectively, but the only 1,3-bisketenes which have been reported are the rather unstable C_5O_2[1e,f] and a dicationic species claimed[1c] to be formed from an azulene dicarboxylic acid. Several 1,4-bisketenes have been prepared, as reviewed elsewhere.[2a,b]



1

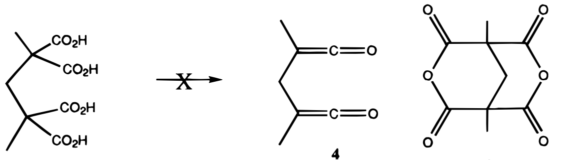
O=C=C=O

2

O=C=C=C=O

3

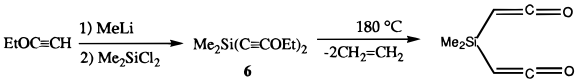
In 1923 Staudinger and Kreis reported an unsuccessful attempt to prepare the 1,3-bisketene **4** by dehydration and decarboxylation of the bis(malonic acid) **2** (eq 1)[1a] but obtained only the bis(anhydride) **5**. We now report the first preparation and spectroscopic characterization of a *bona fide* 1,3-bisketene which is stable and persistent and the first trisketene. These syntheses are based on the proposition that the ketenyl groups in a 1,3-bisketene such as **4** would be constrained to a geometry such that intramolecular cyclization of the ketenyl groups is not feasible, so that these species would be isolable if they could be generated.



(1)

4 **5**

Ketene formation from pyrolysis of alkynyl ethers[2a] offered the prospect of an efficient route to 1,3-bisketenes, and this strategy has been vindicated. Thus reaction of lithium ethoxyacetylide with dimethylsilyl dichloride gave 60% of dimethylbis(ethoxyethynyl)silane **6**,[3a] which on pyrolysis at 180 °C in a gas chromatograph gave a 75% yield of bis(2-oxoethenyl)dimethylsilane (**7**)[3b] (eq 2).



(2)

7

Evidence for the structure of **7** comes from the ketenyl IR bands at 2108 and 2129 cm^{-1} and from the NMR spectra. We have recently reported[4a] a survey of NMR chemical shifts of silylated ketenes, and the most diagnostic shifts of **7** in $CDCl_3$ may be compared to those of $Me_3SiCH{=}C{=}O$ (parentheses): ^{13}C NMR δ C_α, 178.8 (179.2); C_β 0.9 (−0.2); ^{17}O δ 260.1 (255.0); ^{29}Si δ −3.3 (−0.2). The shifts are all characteristic of silylketenes and differ from those of other ketenes or related molecules.[4a] The UV $\lambda_{max}^{isooctane}$ of **7** of 300 nm ($\epsilon = 88$) may be compared to that for *t*-$BuMe_2SiCH{=}C{=}O$, λ_{max}^{hexane} 292 ($\epsilon = 35$).[2a] That the λ_{max} for **7** is shifted only 8 nm to longer wavelength and that the extinction coefficient for **7** (two ketenyl groups) is only 2.5 times greater suggest that there is perhaps a modest conjugative interaction between the two ketenyl groups in **7** separated by a Si atom. A similar situation was found for silicon substituted with one and two vinyl groups and was taken as evidence of the absence of conjugation between the vinyl groups through the silicon atoms.[4b] It has been argued that conjugation between silicon d orbitals and p orbitals of second period elements is relatively unimportant,[4c−e] but this question is still under investigation.[4f]

A procedure analogous to that used to prepare **7** gave a 56% yield of methyltris(ethoxyethynyl)silane **8**,[5a] which upon gas chromatographic pyrolysis at 180 °C gave an 82% yield of the trisketene **9**[5b] (eq 3). The spectral characteristics of the trisketene **9** are analogus to those of the bisketene **7** and are distinguished by almost additive shifts by δ 3.8 ± 0.7 to higher field in the ^{29}Si NMR and to longer λ by 7.5 ± 0.5 nm in the UV for additional ketenyl groups in the tris- and bisketene compared to *t*-$BuMe_2SiCH{=}C{=}O$, respectively, and negligible differences in the ^1H, ^{13}C, and ^{17}O NMR.

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(2) (a) Tidwell, T. T. *Ketenes*; Wiley, New York, 1995. (b) Allen, A. D.; Ma, J.; McAllister, M. A.; Tidwell, T. T.; Zhao, D.-c. *Acc. Chem. Res.* **1995**, *28*, 265−271. (c) Allen, A. D.; Colomvakos, J. D.; Egle, I.; Lusztyk, J.; McAllister, M. A.; Tidwell, T. T.; Wagner, B. D.; Zhao, D.-c. *J. Am. Chem. Soc.* **1995**, *117*, 7552−7553. (d) McAllister, M. A.; Tidwell, T. T. *J. Am. Chem. Soc.* **1994**, *116*, 7233−7238. (e) Zhao, D.-c.; Allen, A. D.; Tidwell, T. T. *J. Am. Chem. Soc.* **1993**, *115*, 10097−10103. (f) Allen, A. D.; Ma, J.; McAllister, M. A.; Zhao, D-c. *J. Chem. Soc., Perkin Trans. 2* **1995**, 847−851.

(3) (a) IR (film) 2178 cm^{-1} (C≡C); ^1H NMR ($CDCl_3$) δ 0.26 (s, 6, Me_2Si), 1.38 (t, 6, $J = 7.1$ Hz, $2CH_3$); 4.16 (q, 4, $J = 7.1$ Hz, $2CH_2$); ^{13}C NMR ($CDCl_3$) δ 1.9, 14.2, 35.4, 74.9, 109.3; EIMS *m/z* 196 (M^+, 0.2), 181 ($M^+ - CH_3$, 28), 153 ($M^+ - C_2H_4 - CH_3$, 33), 125 ($M^+ - 2C_2H_4 - CH_3$, 100), 99 ($M^+ - 2C_2H_4 - CH{=}C{=}O$, 32); HRMS *m/z* calcd for $C_{10}H_{16}O_2Si$, 196.0920; found, 196.0911. (b) IR (isooctane) 2129, 2108 cm^{-1} (C═C═O); ^1H NMR ($CDCl_3$) δ 0.34 (s, 6, Me_2Si), 1.96 (s, 2, CH═C); ^{13}C NMR ($CDCl_3$) δ 0.9 (CH); 1.2 (CH_3), 178.8 (C═O); ^{17}O NMR ($CDCl_3$) δ 260.1; ^{29}Si NMR ($CDCl_3$) δ −3.3; UV $\lambda_{max}^{isooctane}$ 300 nm ($\epsilon = 88$); EIMS *m/z* 140 (M^+, 33), 125 ($M^+ - CH_3$, 100), 99 ($M^+ - C_2HO$, 26), 69 ($M^+ - C_3H_3O$, 24); HRMS *m/z* calcd for $C_6H_8SiO_2$, 140.0293; found, 140.0300.

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(5) (a) IR (film) 2171 cm^{-1} (C≡C); ^1H NMR ($CDCl_3$) δ 0.37 (s, 3, MeSi), 1.38 (t, 9 $J = 7.0$ *Hz*, $3CH_3$); 4.18 (q, 6, $J = 7.0$ *Hz*, 3 CH_2); ^{13}C NMR ($CDCl_3$) δ 3.6, 14.4, 34.6, 75.2, 109.2 EIMS *m/z* 235 ($M^+ - CH_3$, 25), 151 ($^+Si(CH{=}C{=}O)_3$, 100); HRMS *m/z* calcd for $C_{12}H_{15}O_3Si$, 235.0790; found, 235.0784. (b) IR (isooctane) 2136, 2108 cm^{-1} (C═C═O); ^1H NMR ($CDCl_3$) δ 0.48 (s, 3, CH_3), 2.10 (s, 3, CH═C); ^{13}C NMR ($CDCl_3$) δ 1.8 (CH), 2.0 (CH_3), 178.0 (C═O); ^{17}O NMR ($CDCl_3$) 263.9; ^{29}Si NMR ($CDCl_3$) $\delta = -7.87$; UV $\lambda_{max}^{isooctane}$ 307 nm (ϵ 170); EIMS *m/z* 166 (M^+, 54), 151 ($M^+ - CH_3$, 100), 125 ($M^+ - CH_3$, 54); HRMS *m/z* calcd for $C_6H_6O_3Si$ 150.9851; found, 150.9843.

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$$\mathrm{EtOC{\equiv}CLi} \xrightarrow{\mathrm{MeSiCl_3}} \underset{\mathbf{8}}{\mathrm{MeSi(C{\equiv}COEt)_3}} \xrightarrow[-3\ \mathrm{CH_2{=}CH_2}]{180\ ^\circ\mathrm{C}} \underset{\mathbf{9}}{\mathrm{MeSi(CH{=}C{=}O)_3}} \quad (3)$$

Calculations using Gaussian 92[6] at the RHF/6-31G*//RHF/6-31G* + ZPVE level of the structure of $SiH_2(CH{=}C{=}O)_2$ (**10**) and $SiH(CH{=}C{=}O)_3$ (**11**), which should be reasonable models for **7** and **9**, respectively, reveal at least two minimum energy conformations for each, as shown in Figure 1. For the bisketene these are the *anti*-conformation **10a**, slightly distorted from C_2 symmetry, and the *syn*-conformation **10b**, slightly distorted from C_s symmetry, which is calculated to be 0.75 kcal/mol higher in energy than **10a**. For the trisketene the C_3 or propellar conformation **11a** is 2.6 kcal/mol more stable than the C_{3v} or crown conformation **11b**. Some salient bond distances and bond angles for **10a,b** and **11a,b** are given in Table 1 (supporting information), and these tend to be quite similar. There are significant differences in the calculated dipole moments, which are 0.99 and 2.59 D for **10a,b**, respectively, and 2.45 and 3.71 D for **11a,b**, respectively.

The calculated values of the isodesmic exchange reactions of eqs 4 and 5 are 2.01 and 4.77 kcal/mol, respectively,[7] suggesting that there is a net stabilization for the disproportionation of the monoketene $SiH_3CH{=}C{=}O$ into SiH_4 and the bisketene **10a** and trisketene **11a** of about 2.4 ± 0.4 kcal/mol for each successive ketenyl group. However, the conversion of eq 6, in which the silicon remains disubstituted, is thermoneutral. Taken together these data suggest that there is no diminution of the ability of silicon to stabilize ketenes even when a second or third such moiety is added.

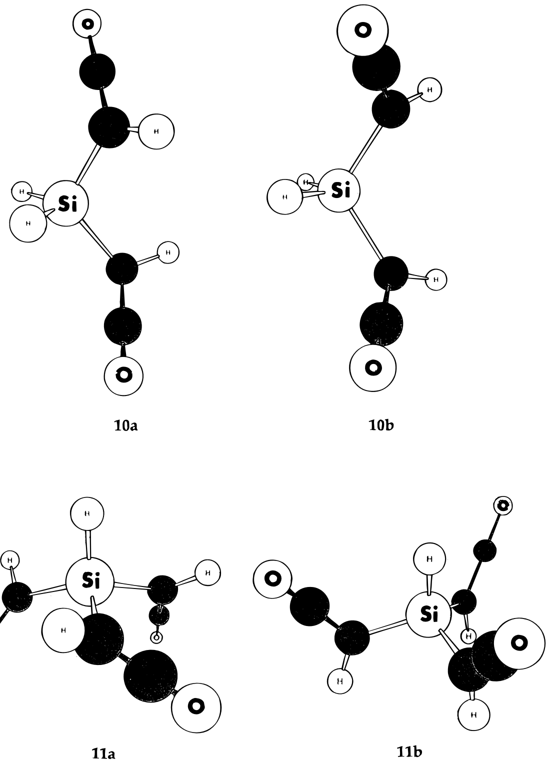
$$\underset{\mathbf{10a}}{\mathrm{SiH_2(CH{=}C{=}O)_2}} + \mathrm{SiH_4} \xrightarrow[2.01\ \mathrm{kcal/mol}]{\Delta E\,=} 2\mathrm{SiH_3CH{=}C{=}O} \quad (4)$$

$$\underset{\mathbf{11a}}{\mathrm{SiH(CH{=}C{=}O)_3}} + 2\mathrm{SiH_4} \xrightarrow[4.77\ \mathrm{kcal/mol}]{\Delta E\,=} 3\mathrm{SiH_3CH{=}C{=}O} \quad (5)$$

$$\underset{\mathbf{10a}}{\mathrm{SiH_2(CH{=}C{=}O)_2}} + \mathrm{SiH_2(CH_3)_2} \xrightarrow[0.00\ \mathrm{kcal/mol}]{\Delta E\,=} 2\mathrm{SiH_2(CH_3)(CH{=}C{=}O)} \quad (6)$$

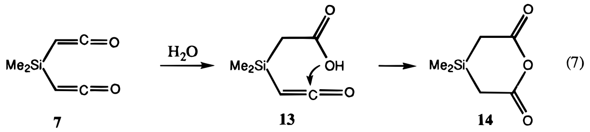
The reactivity of **7** toward H_2O at 25 °C was measured in $H_2O{-}CH_3CN$ mixtures by monitoring the decrease in the UV spectrum at 300 nm as we have done for other ketenes[2e] and showed a single first-order rate process.[8] Careful reaction of **7** with 5% H_2O in 1/1 $CHCl_3/CH_3CN$ and recrystallization gave 40% of the acid $Me_2Si(CH_2CO_2H)_2$ (**12**),[9] but at higher concentrations of H_2O **12** was unstable.

No other rate process was visible, and so it appears that hydration of the second ketenyl group in **7** proceeds at least as fast as the first. A possible pathway would involve initial formation of the ketenyl carboxylic acid **13**, which could react intramolecularly to give the acid anhydride **14** and then the diacid **12** (eq 7). In the hydration of the 1,2-bisketene **1** (R = Me_3Si), an intermediate ketenyl carboxylic acid was observed and characterized.[2e,f]


10a 10b

11a 11b

Figure 1. Calculated (RHF/6-31G*) conformations: of $SiH_2(CH{=}C{=}O)_2$ **10a** (*anti*), **10b** (*syn*) and of $SiH(CH{=}C{=}O)_3$ **11a** (propellar), **11b** (crown).



7 **13** **14**

The hydration rate of **7** in $H_2O{-}CH_3CN$ as a function of H_2O concentration parallels those of the bisketene $(Me_3SiC{=}C{=}O)_2$ (**1**, R = Me_3Si) and the monoketenes $Me_3SiCH{=}C{=}O$ and $t\text{-}BuMe_2SiCH{=}C{=}O$, but **7** is more reactive than these in 33.3 M H_2O by factors of 3.0, 10, and 33, respectively. The detailed mechanism of hydration of **7** and the causes of its high reactivity are under further study.

The route used for the preparation of **7** and **9** appears capable of extension to the preparation of other polyketenes, and efforts in this direction are underway, as are studies of other reactions of these species.

Acknowledgment. Financial support by the Natural Sciences and Engineering Research Council of Canada and the Ontario Centre for Materials Research is gratefully acknowledged.

Supporting Information Available: Salient energies, bond distances, and bond angles for **10a,b** and **11a,b** (1 page). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[6] Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92, Revision C*; Gaussian Inc.: Pittsburgh, PA, 1992.

[7] Based on RHF/6-31G*//RHF/6-31G* + ZPVE calculated energies of **10a**, **11a**, $SiH_3CH{=}C{=}O$, SiH_4, SiH_3CH_3, and $SiH_2(CH_3)_2$ of -592.3494, −742.9294, −441.7706, −291.1950, −330.2137, and −369.2330 hartees, respectively.

[8] k_{obs} (s^{-1}) × 10^2 and $[H_2O]$ (M) in H_2O/CH_3CN (parentheses): 6.83 (33.3), 3.34 (27.8), 1.73 (22.2), 0.957 (16.7), 0.390 (11.1); $\log k_{obs} = 0.0546\,[H_2O] - 2.98$ ($r = 0.998$).

[9] Mp 130 °C; IR (KBr) 3240−2760 (broad, CO_2H), 1714 cm^{-1} (C=O); 400 MHz ^1H NMR (CD_3CN) δ 0.19 (s, 6, $2CH_3$), 1.96 (s, 4, $2CH_2$), 8.90 (broad s, 2, CO_2H); ^{13}C NMR (CD_3CN) δ −3.12, 25.36, 173.85; EIMS *m/z* 175 ($M^+ - H$, 2), 133 ($M^+ - C_2H_3O$, 19), 117 ($M^+ - C_2H_3O_2$, 36), 75 ($SiO_2CH_3^+$, 100), CIMS *m/z* 177 ($M^+ + 1$); HRCIMS *m/z* calcd for $C_6H_{13}O_4Si$, 177.0583; found, 177.0593.